STUDIES ON AMINO-ACIDS AND RELATED COMPOUNDS. PART VII. ON THE OXIDATION OF VARIOUS AMINO-ACIDS.

By Yoshitaro TAKAYAMA.

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Amino-acids occurring in nature can be represented by the general formula $R(NH_2)\cdot COOH$. R denotes diverse radicals of aliphatic, aromatic and heterocyclic fields, functional group of which varies from acidic, neutral to basic. In addition to these, the two compounds having imino-group, namely proline and oxyproline, are obtained from the hydrolysate of protein.

Many paper[1] have been published on the oxidation of amino-acids by various oxidising agents. But in almost all of these it is discussed merely on the first stage of oxidation (oxidation of α-amino-group), and the changes of the radical R are left untouched.

Recently F. Lieben and E. Molner[2] oxidised many amino-acids with a mixture of potassium bichromate and sulphuric acid and from the results of their oxidation they classified the amino-acids into three groups as follows:

(1) Glycine, leucine, aspartic acid, arginine, cystine, tyrosine and tryptphane.
(2) Alanine, glutamic acid and valine.
(3) Proline, histidine and lysine.

The author reported several studies on the electrolytic oxidation of seven kinds of amino-acids including some of their related compounds, and observed that at the equal consumption of electricity the amounts of decomposed amino-acids widely differed according to their kinds. This difference may be attributed to the relative oxidisability of the group R in the acid. Now the author intends to investigate more scrupulously the oxidation of these compounds by the following experiments.

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(1) A. Strecker, *Ann.*, **123**(1862), 363; K. Langheld, *Ber.*, **42** (1909), 392, 2360; H. D. Dakin, T. B. Cohen, M. Daufresne and J. Kenoyon, *Chem. Abstract*, **10** (1916) 2912; H. Wieland und E. Bergel, *Ann.*, **439** (1924), 196; S. Goldschmidt und W. Beuschel, *Ann.*, **447** (1926), 197.

(2) F. Lieben und E. Molnar, *Monatsh.*, **53-54** (1929), 1–13.

More than ten of the amino-acids having various structure were selected and they were electrolysed under the same conditions. During the course of electrolysis the amounts of carbon dioxide and ammonia produced were measured from time to time. The experiments were carried out with following substances, those with similar structure being taken in pair in each case.

Monoamino-carboxylic acids:

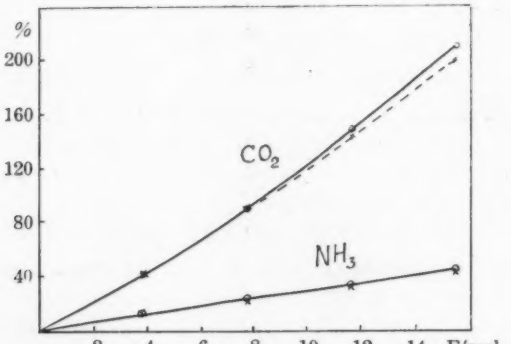
Glycine, alanine, valine, leucine (aliphatic);
Aspartic acid, glutamic acid (aliphatic dicarboxylic);
Tyrosine, phenylalanine (aromatic);
Proline, pyrrolidone-carboxylic acid (heterocyclic);

Diamino-carboxylic acids and others:

Lysine (aliphatic);
Tryptophane, imidazolyl-propionic acid and histidine (heterocyclic).

Electrolytic conditions. 10 Millimols of the sample are dissolved in 30 c.c. of 2N.-sulphuric acid. C.D.: 2 amp./dm^2., electrodes: lead peroxide anode and lead cathode.

Tyrosine and Phenylalanine. (Fig. I). The curves representing the course of formation of carbon dioxide and ammonia from these amino-acids nearly coincide with each other. The curves of tyrosine always lie slightly above those of phenylalanine. The same results were discussed in a previous paper.[3]

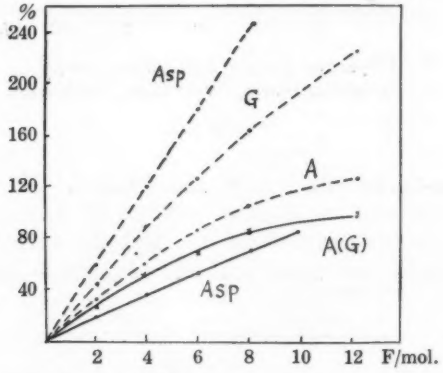


○ Tyrosine. × Phenylalaine.

Fig. I.

(3) Part V. This Bulletin, **8** (1933), 178.

Alanine,[4] Glutamic Acid[5] and Aspartic Acid. (Fig. II). NH_3-curves of the former two are in good coincidence, but some difference is observed between their CO_2-curves. This fact may be explained as follows. α-Oxidation of the two amino-acids proceeds at equal rate, and alanine gives acetic acid while glutamic acid gives succinic acid, and the latter is less stable to oxidation than the former. CO_2 formed in excess in the case of glutamic acid is due to the more readiness to oxidation of succinic acid. NH_3-curve of aspartic acid lies below the above two, and CO_2-curve, on the contrary, lies far above. Aspartic acid gives the highest yield of CO_2, which may be explained by the fact that its oxidation product (malonic acid) is markedly unstable towards oxidation.



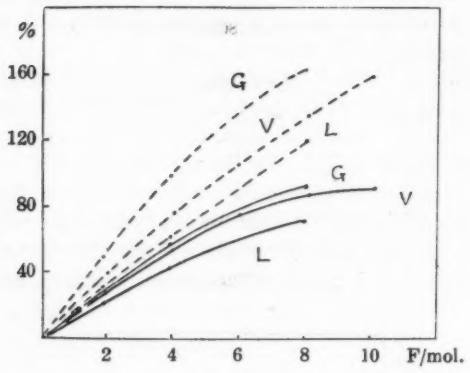
CO_2-curves (----), NH_3-curves (——).
Asp=aspartic acid, G=glutamic acid (×), A=alanine.

Fig. II.

Glycine, Leucine[4] and Valine. (Fig III). NH_3-curves of glycine and valine belong to the same type as that of alanine. In the case of leucine it lies considerably beneath that of alanine. CO_2-curves of these compounds lie above that of alanine. The result shows that the radical R in leucine is less stable to anodic oxidation as Fichter has pointed out.

$$(CH_3)_2CH\cdot CH_2CH(NH_2)COOH \rightarrow (CH_3)_2CH\cdot CH_2\cdot COOH + CO_2 + NH_3$$
$$\downarrow$$
$$(CH_3)_2CH\cdot COOH$$
$$\downarrow$$
$$(CH_3)_2CO \qquad \text{(Fichter)}^{[4]}$$

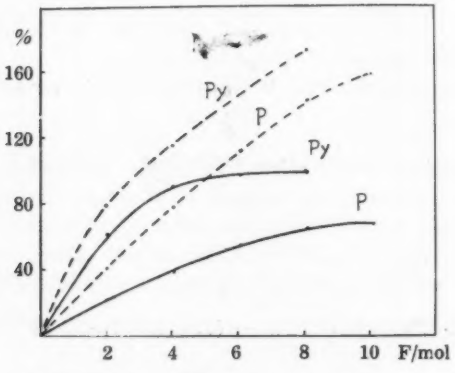
(4) Fr. Fichter und F. Kuhn, *Helv. chim. Acta*, **7** (1924), 167.
(5) Part. I. This Bulletin, **8**(1933), 125.



CO_2-curves (----), NH_3-curves (——).
G=glutamic acid, V=valine, L=leucine.

Fig. III.

Pyrrolidone-Carboxylic Acid[6] **and Proline.** (Fig. IV). NH_3-curve of the former occupies the highest position of those of all amino-acids, and that of proline is apart from it. But the author, in fact, isolated succinimide from the oxidation products of proline—the same product as

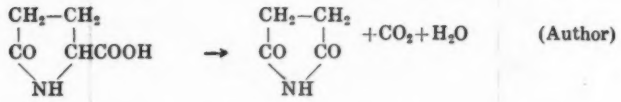


CO_2-curves (----), NH_3-curves (——).
Py=pyrrolidone-carboxylic acid, P=proline.

Fig. IV.

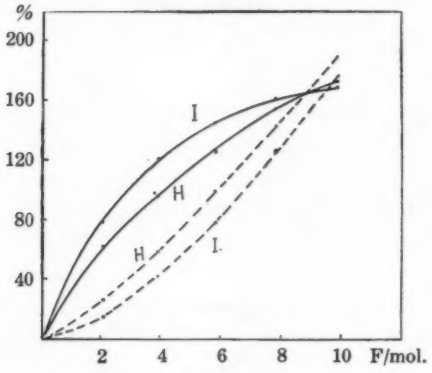
(6) Part. II. This Bulletin, **8** (1933), 137.

from pyrrolidone-carboxylic acid. The similar type of oxidation may proceed in these compounds, though somewhat different in rate.



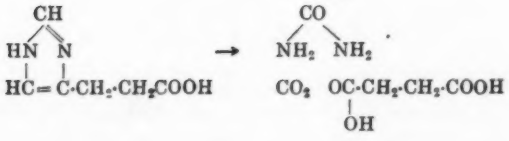
(Author)

Histidine and Imidazolyl-Propionic Acid.[7] (Fig. V). NH_3-curves and CO_2-curves of these compounds present the similar type. On oxidation, these compounds are easily attacked at their imidazol nucleus, and it is observed that a considerable amount of urea was also formed from histidine. Further works on histidine and proline are now in progress.



NH_3-curves (——), CO_2-curves (- - - -).
I=imidazolyl-propionic acid, H=histidine.

Fig. V.



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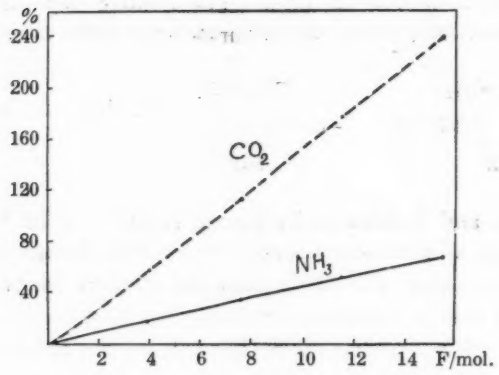
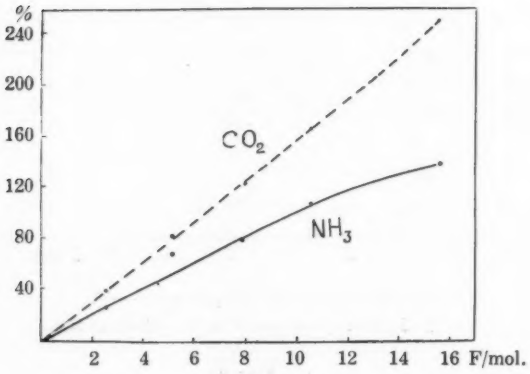
Tryptophane and Lysine. (Fig. VIa, VIb). CO_2-curves of these compounds lie not far away from each other.

(7) Part VI. This Bulletin, 8 (1933), 189.



Tryptophane.

Fig. VIa.



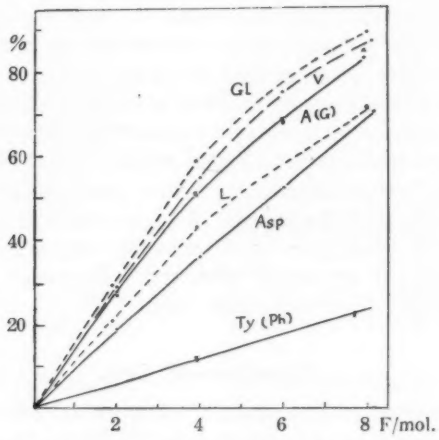
Lysine.

Fig. VIb.

Comparison of the Oxidisability of Monoaminocarboxylic Acids. (Fig. VII). By taking NH_3-curves as a criterion of oxidisability, all amino-acids can be arranged in the following order and divided into three groups.

I) Glycine, valine, glutamic acid and alanine.
II) Leucine and aspartic acid.
III) Tyrosine and phenylalanine.

The members of the first group give curves which are close together, and may be regarded as typical. Curves of the compounds of the third group are completely superposed. Those of the second group are located between the two groups.



Gl=glycine, V=valine, A=alanine, G=glutamic acid (×).
L=leucine, Asp=aspartic acid, Ty=tyrosine, Ph=phenylalnine (×).

Fig. VII.

Colours of the Electrolysates. The electrolysates of some amino-acids are colourless, while those of others are coloured.

(A) Colourless:
Glycine, alanine, valine, leucine, aspartic acid, glutamic acid and pyrrolidone-carboxylic acid.

(B) Coloured, but formation of melanin-like substance is not observed:
Lysine (faint yellow), proline (light brown then colourless).

(C) Dark coloured, and a black melanin (humin) is formed after a certain times:
Tyrosine, phenylalanine (red, then turning to dark brown), tryptophane (dark yellowish brawn), histidine (dark purple).

It is a well known fact that during the hydrolysis of protein a black amorphous powder named humin is formed. According to Roxas[8] following amino-acids have a share in humin formation during the hydrolysis of protein; namely tryptophane, tyrosine, cystine, lysine, arginine, histidine and proline (under a certain condition). Author's results fairly agree with that of Roxas, thus, substances which are classified under (B)

(8) M. L. Roxas, *J. Biol. Chem.*, **27** (1916), 71.

and (C) groups are all those mentioned by Roxas as amino-acids that form humin.

It is cited by many authors that the amino-acids, on oxidation, yield corresponding aldehydes having one atom of carbon less. But in the author's experiments carbonyl compounds are not isolated except in one case, namely imidazolyl-propionic acid. It may be considered that the carbonyl compounds perhaps once formed are soon further oxidised to acids by the vigorous action of lead peroxide anode.

The results of the communications hitherto published may be briefly summarised as follows. Aliphatic α-amino-acids first undergo α-oxidation and produce corresponding aldehydes, which are at once converted into acids. Through further oxidation various products are obtained according to the difference of R-groups. As for aromatic and heterocyclic α-amino-acids, their behaviour on electrolytic oxidation are complicated, and specific groups R are easily attacked. Moreover, these amino-acids produce melanin or humin-like substances.

Experimental Part.

Amino-acids used in this experiment were as follows:

l-Tyrosine, N = 7.76% (calc. for $C_9H_{11}O_3N$, N = 7.74%).
l-Phenylalanine, N = 8.47% (calc. for $C_9H_{11}O_2N$, N = 8.48%).
dl-Alanine (Kahlbaum), N = 15.75% (calc. for $C_3H_7O_2N$, N = 15.73%).
d-Glutamic acid, N = 9.36% (calc. for $C_5H_9O_4N$, N = 9.50%).
Glycine (Merck), N = 18.58% (calc. for $C_2H_5O_2N$, N = 18.67%).
(Kahlbaum) N = 18.66%.
dl-Valine (Eastman), N = 12.27% (calc. for $C_5H_{11}O_2N$, N = 11.96%).
l-Leucine, N = 10.84% (calc. for $C_6H_{13}O_2N$, N = 10.69%).
dl-Aspartic acid (Kahlbaum), N = 10.68% (calc. for $C_4H_7O_4N$, N = 10.53%).
d-Lysine picrate, picric acid = 60.87% (calc. for $C_6H_{14}O_2N_2 \cdot C_6H_3O_7N_3$, picric acid = 61.06%).
l-Tryptophane (Th. Schuchardt), N = 13.42% (calc. for $C_{11}H_{12}O_2N_2$, N = 13.72%).
l-Pyrrolidone-carboxylic acid, N = 10.82% (calc. for $C_5H_7O_3N$, N = 10.85%).
l-Proline (Fraenkel u. Landau), N = 11.96% (calc. for $C_5H_9O_2N$, N = 12.17%).
β-Imidazolyl-propionic acid, N = 19.80% (calc. for $C_6H_8O_2N_2$, N = 19.99%).
l-Histidine dihydrochloride, N = 18.43% (calc. for $C_6H_9O_2N_3 \cdot 2HCl$, N = 18.42%).

Apparatus is shown in Fig. VIII.

Cell: A cylindrical glass vessel of 60 c.c. capacity, provided with a rubber stopper which carries two electrodes and a rubber stoppered tube (C). The latter (C) is used to pass air after every interruption of electrolysis and at the same time to withdraw the solution with a pipette. To the cell was fused a spiral condenser which serves as delivery tube. It was connected to a bubbler (E) by a piece of rubber tubing.

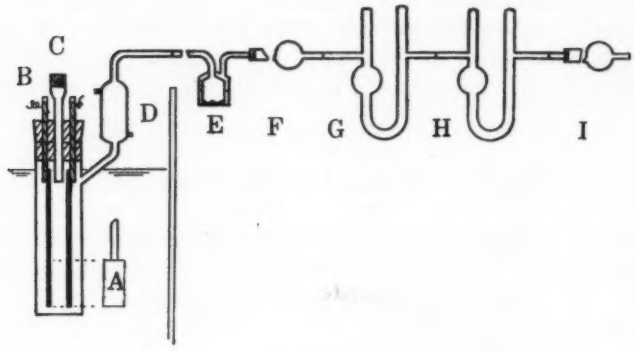


Fig. VIII.

A: Electrodes, lead peroxide anode and lead cathode (2×4 cm.)
B: Brass rods which support electrodes, coated with bakelite varnish.
D: Spiral condenser.
E: Bubbler containing concentrated sulphuric acid.
F: Calcium chloride tube for drying gases.
G and H: Tared absorption tubes for CO_2 containing soda-lime.
I: Calcium chloride guard tube.

Generally ten millimols (in some cases 5 millimols) of amino-acids were dissolved in 30 c.c. of 2N.-sulphuric acid. The solution was electrolysed in the above cell which was kept at a constant temperature (30° or 35°) in a thermostat. Current density was 0.16 amp./2×4 cm. = 2 amp./dm^2. The amount of electricity was determined by copper coulometer.

After every definite consumption of electricity, i.e. 2F/mol, 4 F/mol and so on, electrolysis was interrupted. Air freed from CO_2 was passed through the apparatus from the tube (C) for about half an hour until all of the CO_2 was replaced by air. Soda-lime tubes were weighed. From the increase of weight of these tubes the amount of carbon dioxide formed was estimated and expressed in molar percentage to amino-acid used. 0.2–0.3 c.c. and 0.3–1.0 c.c. of the solution were drawn out with a pipette from the tube (C) and exactly weighed. In the former total-N and in the latter NH_3-N were determined.* After each set of determinations

* Determination of NH_3 was strictly carried out under the following conditions using micro-Kjeldahl apparatus. 5 c.c. of 30% NaOH were added and steam was passed through the solution for ten minutes.

The amount of water decomposed by electrolysis under this condition is ca. 0.09 c.c. for 1F/mol. Thus the loss of water caused by this effect is neglected.

the volume of the solution was diminished by 0.5–1.3 c.c. The current quantity applied before next determination was reduced to such an extent as 2F/mol is maintained in relation to the original volume of the solution. Correction was made to the amount of CO_2 by the same reason.

Table I. Tyrosine and Phenylalanine.

Solutions: 1.8049 gr. (10.04 millimols) of tyrosine in 30 c.c. of 2N.-H_2SO_4; 1.6498 gr. (9.99 millimols) of phenylalanine in 30 c.c. of 2N.-H_2SO_4; Temp.: 35°C.

Subst. millimols.	Faradays per mol.	CO_2 mol %	NH_3-N mg.	Total-N mg.	NH_3-N/Total-N mol %
I Tyrosine 10.04	1.2093 gr. Cu 3.81	0.1753 gr. 39.9	0.448 mg. in 1 c.c.	1.237 mg. in 0.3 c.c.	10.85
I Phenylalanine 9.99	,,	40.1	0.456 1 c.c.	1.240 0.3 c.c.	10.97
II Tyrosine $10.04\times\frac{28.0}{30.0}$	3.87 Total 7.68	49.2 Total 89.1	0.951 1 c.c.	1.262 0.3 c.c.	22.27
II Phenylalanine $9.99\times\frac{28.0}{30.0}$	,,	48.8 / 88.9	0.913 1 c.c.	1.262 0.3 c.c.	21.72
III Tyrosine $10.04\times\frac{26.7}{30.0}$	3.95 / 11.63	59.2 / 148.3	0.726 0.5 c.c.	1.257 0.3 c.c.	34.64
III Phenylalanine $9.99\times\frac{26.7}{30.0}$	,,	53.7 / 142.6	0.688 0.5 c.c.	1.256 0.3 c.c.	32.96
IV Tyrosine $10.04\times\frac{25.9}{30.0}$	3.91 / 15.54	60.7 / 209.0	0.955 0.5 c.c.	1.292 0.3 c.c.	44.34
IV Phenylalanine $9.99\times\frac{25.9}{30.0}$	,,	57.0 / 199.6	0.896 0.5 c.c.	1.264 0.3 c.c.	42.54

Table II. Glutamic Acid and Alanine.

Solutions: 1.4765 gr. (10.04 millimols) of glutamic acid in 30 c.c. of 2N.-H_2SO_4; 0.8917 gr. (10.03 millimols) of alanine in 30 c.c. of 2N.-H_2SO_4; Temp.: 35°C.

Subst. millimols.	Faradays per mol.	CO_2 mol %	NH_3-N mg.	Total-N mg.	NH_3-N/Total-N mol %.
I Glutamic acid 10.04	2.010	42.5	1.111 1 c.c.	0.853 0.2 c.c.	26.0
I Alanine 10.03	,,	32.95	1.231 1 c.c.	0.892 0.2 c.c.	27.6
II Glut. acid $10.04\times\frac{28.8}{30.0}$	3.918	87.53	1.075 0.5 c.c.	0.842 0.2 c.c.	51.0
II Alanine $10.03\times\frac{28.8}{30.0}$	,,	59.91	1.129 0.5 c.c.	0.897 0.2 c.c.	50.4
III Glut. acid $10.04\times\frac{28.1}{30.0}$	5.972	126.8	1.418 0.5 c.c.	0.832 0.2 c.c.	68.1
III Alanine $10.03\times\frac{28.1}{30.0}$	,,	86.11	1.570 0.5 c.c.	0.933 0.2 c.c.	67.3
IV Glut. acid $10.04\times\frac{27.6}{30.0}$	7.950	163.0	1.027 0.3 c.c.	0.808 0.2 c.c.	84.7
IV Alanine $10.03\times\frac{27.6}{30.0}$	,,	104.6	1.168 0.3 c.c.	0.874 0.2 c.c.	82.9
V Glut. acid $10.04\times\frac{27.1}{30.0}$	12.19	224.2	1.145 0.3395 gr.	1.180 0.2220 gr.	97.0
V Alanine $10.03\times\frac{27.1}{30.0}$	,,	125.8	1.348 0.3286 gr.	0.950 0.2211 gr.	95.5

Table III. Valine and Aspartic Acid.

Solutions: 1.1686 gr. (10.03 millimols) of valine in 30 c.c. of 2N.-H_2SO_4; 1.3303 gr. (9.997 millimols) of aspartic acid in 30 c.c. of 2N.-H_2SO_4; Temp.: 35°C.

Subst. millimols.	Faradays per mol.	CO_2 mol %.	NH_3-N mg.	Total-N mg.	NH_3-N/Total-N mol %.
I Valine 10.03	2.014	38.5	1.254 1.032 gr.	1.775 0.4141 gr.	28.4
I Aspartic acid 9.997	,,	59.1	0.860 1.0549 gr.	1.867 0.4296 gr.	18.8
II Valine $10.03\times\frac{28.6}{30.0}$	4.024	75.2	1.231 0.5221 gr.	0.895 0.2067 gr.	54.4
II Aspartic acid $9.997\times\frac{28.6}{30.0}$	,,	119.9	0.831 0.5450 gr.	0.902 0.2111 gr.	35.7
III Valine $10.03\times\frac{27.9}{30.0}$	6.031	106.6	1.632 0.5247 gr.	0.881 0.2130 gr.	75.2
III Aspartic acid $9.997\times\frac{27.9}{30.0}$	,,	179.6	1.155 0.5306 gr.	0.891 0.2128 gr.	52.1
IV Valine $10.03\times\frac{27.2}{30.0}$	8.135	135.8	1.885 0.5135 gr.	0.938 0.2222 gr.	87.0
IV Aspartic acid $9.997\times\frac{27.2}{30.0}$	,,	243.6	1.497 0.5249 gr.	0.856 0.2112 gr.	70.3
V Valine $10.03\times\frac{26.5}{30.0}$	10.17	156.8	2.070 0.5236 gr.	0.948 2.070 gr.	91.2
V Aspartic acid $9.997\times\frac{26.5}{30.0}$	,,	303.3	1.792 0.5210 gr.	0.838 0.2131 gr.	87.2

Table IVa. Glycine and Leucine.

Solutions: 0.7553 gr. (10.07 millimols) of glycine in 30 c.c. of 2N.-H_2SO_4; 1.3126 gr. (10.02 millimols) of leucine in 30 c.c. of 2N.-H_2SO_4; Temp.: 35°C.

Subst. millimols.	Faradays per mol.	CO_2 mol %.	NH_3-N mg.	Total-N mg.	NH_3-N/Total-N mol %.
I Glycine 10.07	1.905	48.8	1.277 1.0497 gr.	0.880 0.2118 gr.	29.2
I Leucine 10.02	,,	30.0	0.878 1.0326 gr.	0.859 0.2075 gr.	20.5
II Glycine $10.07\times\frac{28.8}{30.0}$	3.932	98.6	1.231 0.5289 gr.	0.870 0.2199 gr.	58.9
II Leucine $10.02\times\frac{28.8}{30.0}$	,,	62.3	0.938 0.5345 gr.	0.898 0.2200 gr.	43.0
III Glycine $10.07\times\frac{28.1}{30.0}$	8.06	161.5	1.741 0.5298 gr.	0.796 0.2152 gr.	89.1
III Leucine $10.02\times\frac{28.1}{30.0}$	,,	121.6	1.425 0.5110 gr.	0.839 0.2141 gr.	71.2

Table IVb. Glycine and Leucine.

Solutions: 0.7514 gr. (10.01 millimols) of glycine in 30 c.c. of 2N.-H_2SO_4; 1.3087 gr. (9.982 millimols) of leucine in 30 c.c. of 2N.-H_2SO_4; Temp.: 30°C.

Subst. millimols	Faradays per mol.	CO_2 mol %.	NH_3-N mg.	Total-N mg.	NH_3-N/Total-N mol %.
I Glycine 10.01	2.056	45.25	0.568 0.5434 gr.	1.368 0.3332 gr.	25.5
I Leucine 9.982	,,	24.70	0.3180 0.5315 gr.	1.310 0.3285 gr.	15.0

Table IVb.—(*Concluded*)

Subst. millimols	Faradays per mol	CO_2 mol %.	NH_3-N mg.	Total-N mg.	NH_3-N/Total-N mol %
II Glycine $10.01\times\frac{29.2}{30.0}$	4.094	85.33	1.051 0.5430 gr.	1.250 0.3297 gr.	51.1
II Leucine $9.982\times\frac{29.2}{30.0}$	,,	56.85	0.662 0.5298 gr.	1.323 0.3253 gr.	30.7
III Glycine $10.01\times\frac{28.4}{30.0}$	6.170	120.5	1.266 0.5270 gr.	1.253 0.3257 gr.	60.5
III Leucine $9.982\times\frac{28.4}{30.0}$	,,	87.85	0.957 0.5320 gr.	1.323 0.3290 gr.	44.8
IV Glycine $10.01\times\frac{27.6}{30.0}$	8.16	145.2	0.727 0.2199 gr.	1.296 0.3318 gr.	84.7
IV Leucine $9.982\times\frac{27.6}{30.0}$	,,	118.3	0.518 0.2259 gr.	1.294 0.3266 gr.	57.9
V Glycine $10.01\times\frac{27.1}{30.0}$	10.12	161.1	1.215 0.3289 gr.	0.858 0.2226 gr.	95.7
V Leucine $9.982\times\frac{27.1}{30.0}$	,,	145.7	0.830 0.3210 gr.	0.848 0.2175 gr.	66.3
VI Leucine $9.982\times\frac{26.6}{30.0}$	12.24	171.6	0.881 0.3163 gr.	0.868 0.2235 gr.	71.7

Table V. Pyrrolidone-Carboxylic Acid and Proline.

Solutions: 1.2909 gr. (10.00 millimols) of *l*-pyrrolidone-carboxylic acid in 30 c.c. of 2N.-H_2SO_4; 1.1507 gr. (10.00 millimols) of proline in 30 c.c. of 2N.-H_2SO_4; Temp.: 30°C.

Subst. millimols.	Faradays per mol.	CO_2 mol %.	NH_3-N mg.	Total-N mg.	NH_3-N/Total-N mol %
I Pyrrolidone carb. acid 10.00	2.054	74.3	1.462 0.5568 gr.	1.393 0.3238 gr.	60.9
I Proline 10.00	,,	41.3	0.494 0.5420 gr.	0.425 0.100 gr.	21.4
II Pyrrolidone carb. acid $10.00\times\frac{29.2}{30.0}$	4.067	101.5	1.680 0.4280 gr.	1.380 0.3157 gr.	89.7
II Proline $10.00\times\frac{29.2}{30.0}$	,,	77.6	0.668 0.4341 gr.	1.356 0.3210 gr.	36.5
III Pyrrolidone carb. acid $10.00\times\frac{28.5}{30.0}$	6.099	136.0	1.389 0.3288 gr.	0.986 0.2241 gr.	96.1
III Proline $10.00\times\frac{28.5}{30.0}$	,,	111.5	0.738 0.3256 gr.	0.943 0.2205 gr.	54.8
IV Pyrrolidone carb. acid $10.00\times\frac{28.0}{30.0}$	8.031	173.4	1.396 0.3210 gr.	1.470 0.3296 gr.	97.4
IV Proline $10.00\times\frac{28.0}{30.0}$	8.096	142.9	0.895 0.3266 gr.	0.944 0.2290 gr.	66.4
V Proline $10.00\times\frac{27.5}{30.0}$	10.32	158.5	0.965 0.3321 gr.	0.927 0.2165 gr.	68.0

Table VI. β-Imidazolyl-Propionic Acid and Histidine.

Solutions: 1.4013 gr. (10.00 millimols) of imidazolyl-propionic acid in 30 c.c. of 2N.-H_2SO_4; 10 millimols of histidine in 30 c.c. of 2N.-H_2SO_4; Temp.: 30°C.

Subst. millimols.	Faradays per mol.	CO_2 mol %	NH_3-N mg.	Total-N mg.	NH_3-N/Total-N mol %.
I Histidine 10.00	2.072	24.78	0.624 0.2298 gr.	1.446 0.1130 gr.	63.7
I Imidaz. prop. acid. 10.00	,,	13.93	0.724 0.2244 gr.	0.927 0.1107 gr.	76.8
II Histidine $10.00\times\frac{29.7}{30.0}$	3.95	59.60	0.894 0.2210 gr.	0.1610 0.1263 gr.	95.1
II Imidaz. prop. acid. $10.00\times\frac{29.7}{30.0}$	,,	42.00	1.108 0.2219 gr.	1.00 0.1204 gr.	120.5
III Histidine $10.00\times\frac{29.4}{30.0}$	5.830	99.5	1.148 0.2230 gr.	1.436 0.1155 gr.	124.2
III Imidaz. prop. acid $10.00\times\frac{29.4}{30.0}$	,,	78.63	1.345 0.2215 gr.	0.842 0.100 gr.	144.2
IV Histine $10.00\times\frac{29.1}{30.0}$	7.82	143.0	1.336 0.2072 gr.	1.397 0.1120 gr.	155.4
IV Imidas. prop. acid $10.00\times\frac{29.1}{30.0}$	,,	127.9	1.512 0.2180 gr.	0.981 0.1149 gr.	162.4
V Histidine $10.00\times\frac{28.8}{30.0}$	9.94	189.6	1.615 0.2265 gr.	1.361 0.1123 gr.	176.7
V Imidas. prop. acid $10.00\times\frac{28.8}{30.0}$	,,	175.8	1.588 0.2205 gr.	1.044 0.1230 gr.	169.4

Eleven millimols of histidine dihydrochloride were dissolved in 25 c.c. of 2N.-sulphuric acid and sufficient water was added to it. It was distilled under reduced pressure to drive off hydrochloric acid. The above treatment was repeated several times until the solution showed no trace of hydrochloric acid. The solution was made up to 25 c.c. (total-N 455.9 mg.) from which 23.08-c.c. were taken for electrolysis (corresponding to 10 millimols of histidine).

It was ascertained that imidazolyl-propionic acid did not yield ammonia when it was treated with steam in the presence of conc. sodium hydroxide.

The electrolysate of β-imidazolyl-propionic acid assumed yellowish tint as the electrolysis proceeded, it was transparent throughout the whole course. In the case of histidine, dark purple colouration was already observed after an hour and melanine-like substance began to deposit at 4F/mol and adhered to the electrodes.

Table VII. Tryptophane.

Solutions: 1.0200 gr. (5.00 millimols) of tryptophase in 30 c.c. of 2N.-H_2SO_4; Temp.: 35°C.

Subst. millimols	Faradays per mol	CO_2 mol %	NH -N mg.	Total-N mg.	NH_3-N/Total-N mol %
Tryptophane 5	3.88	57.2	0.396 1.094 gr.	0.954 0.2241 gr.	17.0
" $5\times\frac{28.8}{30.0}$	7.55	113.2	0.715 1.0571 gr.	0.835 0.2087 gr.	33.8
" $5\times\frac{27.6}{30.0}$	11.45	176.8	0.556 0.5194 gr.	0.949 0.2278 gr.	51.4
" $5\times\frac{26.9}{30.0}$	15.35	239.6	0.730 0.5244 gr.	0.897 0.2174 gr.	67.4

Table VIII. Lysine.

Solutions: 7.49 millimols of lysine* in 30 c.c. of ca. 2N.-H_2SO_4; Temp.: 35°C.

Subst. millimols.	Faradays per mol	CO_2 mol %.	NH_3-N mg.	Total-N mg.	NH_3-N/Total-N mol %.
Lysine 7.49	2.49	37.6	0.433 0.5 c.c.	0.700 0.1 c.c.	24.6
" $7.49\times\frac{29.4}{30.0}$	5.16	80.1	0.495 0.2 c.c.	1.471 0.2 c.c.	67.2
" $7.49\times\frac{28.4}{30.0}$	7.94	122.2	1.533 0.5 c.c.	1.578 0.2 c.c.	77.8
" $7.49\times\frac{27.7}{30.0}$	10.55	165.0	1.749 0.4 c.c.	1.624 0.2 c.c.	107.8
" $7.49\times\frac{26.7}{30.0}$	15.85	249.8	2.280 0.4 c.c.	1.651 0.2 c.c.	138.2

* 3.75 gr. (10 millimols) of lysine picrate were dissolved in 25 c.c. of 2N.-sulphuric acid. The solution was thoroughly extracted with ether to remove picric acid. By adding 2N.-sulphuric acid the solution was made up to 30 c.c. (content of lysine equals to 7.49 millimols).

In conclusion, the author wishes to express his sincere thanks to Professor K. Matsubara for his kind encouragement and invaluable advices given to these studies. At the same time, the author is also indebted to continuous suggestions of Mr. W. Nagai and untired assistance of Mr. H. Ôeda to complete these studies.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

WATER VAPOUR EQUILIBRIA ON VANADIUM AND ITS OXIDES.

By Masami KOBAYASHI.

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Synopsis.

The oxidation-reduction equilibrium of vanadium has been investigated by the dynamical method of Wartenberg and Aoyama. By the experiment it has been suggested that the chemical changes take place in the two stages under the experimental conditions, and the reactions might be expressed by the following: $V+H_2O \rightleftarrows VO+H_2$ and $2VO+H_2O \rightleftarrows V_2O_3+H_2$. Thermodynamic calculations have been made for the above reactions, and the result of the calculated heats of formation agreed fairly well with that of the determinations made by other investigators.

Introduction.

A reduction equilibrium on chromic oxide was determined by H. v. Wartenberg and S. Aoyama[1] in 1927. The principle applied by these investigators consisted of passing a stream of hydrogen saturated with water vapour of known partial pressure on metallic chromium and the oxidation equilibrium is measured at various temperatures by observing the change in colour which takes place on the surface of the metal due to the process of oxidation and reduction going on by the small quantity of oxygen. Later in 1932, by applying the same principle S. Aoyama and Y. Oka[2] determined the oxidation-reduction equilibrium of manganese, in distilled state. Since vanadium is a very refractory substance, and is hardly reducible like the metals mentioned above, and its oxide is reducible by hydrogen only when the latter is carefully dried[3], it has been attempted by the present writer to measure the oxidation equilibrium of vanadium by the principle described above.

Experimental.

Apparatus. The apparatus used was quite the same as described by Wartenberg and Aoyama in their paper, except the reaction tube and the pump for circulating gas. Instead of a silica-tube, a pyrex glass-tube,

(1) *Z. Elektrochem.*, **33** (1927), 144.
(2) *Nippon Kagaku-kaishi* (*J. Chem. Soc. Japan*), **53** (1932), 417.
(3) H. v. Wartenberg, J. Broy & R. Reinicke. *Z. Elektrochem.*, **29** (1923), 214.

5 cm. in diameter and 50 cm. in length, was used as the reaction tube (Fig. 1). To the lower end of the pyrex tube was attached a glass cap with a side tube for introducing hydrogen having a rubber stopper which is overlaid with mercury, and through which two insulated copper leading rods, each 3 mm. in thickness, were thrust into the pyrex tube. The

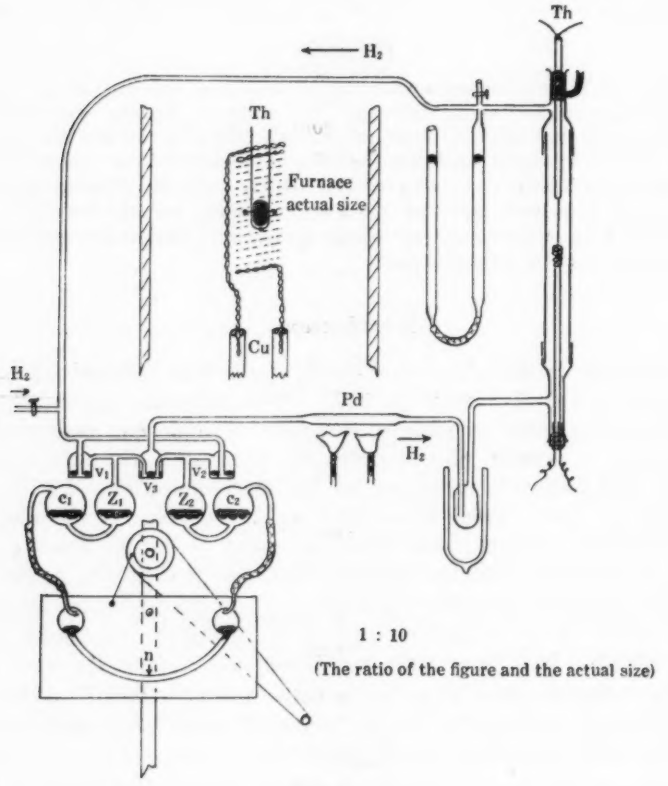

Fig. 1.

joint between the pyrex tube and the glass cap was made tight with picein. A small hole was made at the top of each copper rod to which was inserted each end of molybdenum spiral, of the furnace which is 25 mm. in length, 1 cm. in diameter and 18 turns of the spiral. (Two molybdenum wires each 0.4 mm. in diameter were twisted in making the furnace). On the top of the pyrex tube a glass cap was placed having

an exit tube for hydrogen and also a hanger for a piece of metallic vanadium (3×4×5 mm.). A thermocouple was fused in a glass tube, which is movable through two cork stoppers and is made gas tight with mercury seal. The piece of the metallic vanadium was bound with Pt-wire directly at the junction of the couple.

The pump for circulating gas used in this experiment was a modified form of mercury pump devised by K. Scheel and W. Heuse[4], and had been constructed by Dr. S. Aoyama for his recent experiment on manganese. The mercury pump which has been kindly lent by Dr. Aoyama consists of two glass bulbs Z_1 and Z_2, in which mercury is filled and emptied, alternately, by the pressure due to contraction and expansion of air of constant volume in the communicating bulbs c_1 and c_2. The contraction and expansion of the air are caused by the alternating lateral motion (effected by a motor) of glass tube n, which is half filled with mercury and each end of which is connected to the communicating bulbs with rubber tubes; the mercury in n remains almost stationary even while n moves. If, for example, n inclines to the right, the air in c_1 expands resulting the mercury in Z_1 to be emptied and filling the mercury in c_1. Due to the depression of mercury in Z_1 hydrogen is inhaled through mercury valve v_1; when n inclines to the left the hydrogen is puffed off through mercury valve v_3. Hydrogen passes then over Pd-asbestos heated at about 200°C., and then through the trap dipped in a Dewar's beaker into the pyrex tube and from here returns again to Pd-asbestos through the pump, with a current velocity of about 200 c.c. per minute. The communicating tube of mercury serves to keep the pressure in the closed system at one atmospheric pressure when the furnace is heated at high temperatures.

The furnace was heated by an electric current; a temperature of 1300°C. has been obtained by a current of 18 amperes at 24 volts:

Bath. The temperatures of the bath applied were:

−78.5°C. (carbon dioxide-alcohol),
−19.5°C. (sodium chloride-ice mixtures),
−37.0°C. (melting mercury) } frozen by pouring liquid air drop by drop on mercury
−47.0°C. (solid mercury) } and kept it constant temperature within ±0.3°C. by
−57.0°C. („) } hand regulation,

corresponding respectively to $p_{H_2O} = 6.65 \cdot 10^{-7}$ atm. press.[5]; $1.07 \cdot 10^{-3}$, $1.76 \cdot 10^{-4}$, $5.53 \cdot 10^{-5}$, $1.45 \cdot 10^{-5}$ atm. press.[6]

(4) *Ann. Phys.*, **40** (1913), 474.
(5) Vapour pressure of H_2O, Daudt, *Z. Physik. Chem.*, **106** (1923), 263.
(6) „ „ „ Landolt Börnstein Roth/Scheel, Hw., II, 1315.

Material. The vanadium was prepared by the Goldschmidt method, using 100 parts V_2O_5, 40 parts Al, and 12 parts Na_2CO_3 as flux[7] in an alundum crucible lined with pure magnesia, and the chemical analysis indicates:

Slag (mainly Al_2O_3)	V	Al	Fe
1.4	97.0	1.5	0.4

Results.

Preliminary Experiments. By the use of the apparatus described above some preliminary experiments were carried out as to see whether vanadium metal could be distinguished merely by its appearance from its oxide that has been produced when the metal was heated at various temperatures in an atmosphere of hydrogen saturated with water vapour of very small partial pressure. In the first experiment, the temperature of the bath was kept at –19.5°C. (sodium chloride-ice mixtures), and vanadium was heated at 1000°C. for 2 hours. After cooling it was found that the silver-white metallic surface altered to black. As the temperature of the furnace was then raised to 1050°C. and maintained at this temperature for half an hour, the colour of the metallic surface became darker. After the temperature was raised to and maintained at 1150°C. for an hour, it was found that the colour faded to grey. Then, it was again heated at the same temperature for an another hour, but no change in colour was noticed. In spite of the fact that the heating temperature was further raised about every 100°C. up to 1550°C., and the time for maintaining each temperature was set to about 3 hours, it still remained grey; thus an attempt to reduce the metal to its initial condition was proved unsuccessful, since it was found experimentally difficult to maintain the heating for so many hours at such an elevated temperature as above 1550°C. In the second experiment, the temperature of the bath was lowered and kept at –78.5°C. (carbon dioxide-alcohol), and a different piece of vanadium metal was heated at 1400°C. for an hour and a half. This time no physical change has been observed upon the metal. The temperature was then lowered to 1000°C. and maintained at this temperature for a quarter of an hour. During this time the colour of the surface changed to faint grey. The temperature was, therefore, again raised to 1100°C., and after being maintained at this temperature for an hour, it was reduced to its original condition. When the metal was heated at 900°C. for half an hour, it was again tinged with grey. The colour

(7) M. Oya, *Sci. Rep., Tohoku Imp. Univ., Japan*, **19** (1930), 236.

was still unchanged after the heating had been continued for further 3 hours under the same temperature. In order to see whether it would be darkened in colour at the lower temperatures, as might have been expected from the above first preliminary experiment, the temperature was lowered about 100°C. at a time. At 600°C. it remained grey, in spite of the fact that the heating had been continued for 20 hours; while after 20 hours' heating at 500°C., it was recognized undoubtedly that the grey colour changed to black.

It will be obvious from the above experiments that there must be two different forms of vanadium oxides under the present experimental conditions. It can be stated that they are in equilibrium with each other, besides vanadium with the lower oxide. It is also found that the equilibrium temperatures of carbon dioxide-alcohol bath (–78.5°C.) are between 500 and 600°C. and also 1000 and 1100°C.

Among the following well known vanadium oxides[8], VO (or V_2O_2), V_2O_3, V_2O_4 and V_2O_5, the last two are easily reduced to V_2O_3 by dry hydrogen[9], and, moreover, according to H. Müller[10] the values of $K = p_{H_2O}/p_{H_2}$ in the V_2O_4/V_2O_3-reaction, $V_2O_3+H_2O \rightleftarrows V_2O_4+H_2$, are to be 2.20–5.03 over the range of temperature 493–606°C, and the values of K in the V_2O_5/V_2O_4-reaction, $V_2O_4+H_2O \rightleftarrows V_2O_5+H_2$, are to be 7.6–23.3 over the range of temperature 496–600°C. In the present experiment the values of $K = p_{H_2O}/p_{H_2} = p_{H_2O}/1 = 10^{-7} \sim 10^{-3}$ as it has been described above. Therefore, under the present experimental conditions these oxides are considered to be out of question, and it is assumed that the reactions may be expressed by (I) and (II), as follows:

$$\text{(I)} \quad V+H_2O \rightleftarrows VO+H_2 \qquad \text{and}$$

$$\text{(II)} \quad 2VO+H_2O \rightleftarrows V_2O_3+H_2.$$

This must yet be confirmed by the calculation of thermal values of the reactions. This calculation will be described subsequently.

Final Experiments. Now then, the equilibrium temperatures of both reactions were measured at the bath temperatures mentioned above. Each equilibrium temperature of oxidation and reduction was obtained as the mean of adjacent temperatures within about 20°C.

The results are shown in Tables 1 and 2. The experimental results are best detected by the fact that in each reaction the relation between

(8) J. W. Mellor, *Comp. Treat. Inorg. Chem.*, **9** (1929), 739.
(9) cf. (8) p. 741, 744.
(10) W. Biltz's Festschrift, Hannover (1927); cf. (8) p. 741, 744.

Table 1.

$V+H_2O \rightleftarrows VO+H_2$;

(i) Bath –78.5°C.

Thermoelec. force millivolts	Initial colour of V	Result	Concluded to be
10.7	silver-white	after 4 hrs. grey	oxidation
11.8	grey	,, 2 ,, silver-white	reduction
11.0	faint grey	,, 5 ,, grey	oxidation
11.2	grey	,, 3 ,, silver-white	reduction

Equilibrium temperature between 11.0 and 11.2 = 11.1 millivolts = 1052°C.

(ii) Bath –57.0°C.

12.8	faint grey	after 2 hrs. grey	oxidation
14.2	grey	,, 3 ,, silver-white	reduction
14.0	silver-white	,, 4 ,, grey	oxidation
14.9	grey	,, 1.5,, silver-white	reduction

Equilibrium temperature between 14.0 and 14.2 = 14.1 millivolts = 1268°C.

(iii) Bath –47.0°C.

15.6	silver-white	after 3.5 hrs. grey	oxidation
16.7	grey	,, 1 ,, silver-white	reduction
15.9	silver-white	,, 1 ,, grey	oxidation
16.1	grey	,, 2 ,, silver-white	reduction

Equilibrium temperature between 15.9 and 16.1 = 16.0 millivolts = 1397°C.

$$2\,VO + H_2O \rightleftarrows V_2O_3 + H_2;$$

(i) Bath –78.5°C.

Thermoelec. force millivolts	Initial colour of V	Result	Concluded to be
4.6	faint grey	after 6 hrs. grey	
4.9		,, 18 ,, black	oxidation
5.5	black	,, 20 ,, grey	reduction
4.4	grey	,, 20 ,, black	oxidation
5.1	black	,, 24 ,, grey	reduction

Equilibrium temperature between 4.9 and 5.1 = 5.0 millivolts = 550°C.

(ii) Bath –57.0°C.

6.7	grey	after 2.5 hrs. black	oxidation
7.3	black	,, 1.5 ,, grey	reduction
6.5	grey	,, 3 ,, black	oxidation
6.9	black	,, 2 ,, grey	reduction

Equilibrium temperature between 6.7 and 6.9 = 6.8 millivolts = 710°C.

(iii) Bath –37.0°C.

8.5	grey	after $1\frac{1}{4}$ hrs. black	
8.8		,, 1 ,, more black	oxidation
9.4	black	,, $\frac{1}{2}$,, grey	reduction
9.1	,,	,, 1.5 ,, grey	,,
8.9	grey	,, 2 ,, black	oxidation

Equilibrium temperature between 8.9 and 9.1 = 9.0 millivolts = 890°C.

(iv) Bath –19.5°C.

11.8	grey	after 2 hrs. black	oxidation
12.8	black	,, 1 ,, grey	reduction
12.4	,,	,, 2 ,, grey	,,
12.0	,,	,, 3 ,, grey	,,

Equilibrium temperature between 11.8 and 12.0 = 11.9 millivolts = 1112°C.

Table 2.

a) $Kp_{\cdot 1}$-values and equilibrium temps. for V/VO.

Bath (°C)	$K_{p\cdot 1}$	log $K_{p\cdot 1}$	Temp. C°	T	$1/T$
−78.5	$6.65\cdot10^{-7}$	−6.1772	1052	1325	0.0007547
−57.0	$1.45\cdot10^{-5}$	−4.8394	1268	1541	6489
−47.0	$5.53\cdot10^{-5}$	−4.2576	1397	1670	5988

b) $Kp_{\cdot 2}$-values and equilibrium temps. for VO/V_2O_3.

Bath (°C)	$K_{p\cdot 2}$	log $K_{p\cdot 2}$	Temp. C°	T	$1/T$
−78.5	$6.65\cdot10^{-7}$	−6.1772	550	823	0.0012150
−57.0	$1.45\cdot10^{-5}$	−4.8394	710	983	10172
−37.0	$1.76\cdot10^{-4}$	−3.7537	890	1163	08598
−19.5	$1.07\cdot10^{-3}$	−2.9723	1112	1385	07220

the logarithms of equilibrium constants ($\log K_p = p_{H_2O}/p_{H_2}$) and the reciprocals of absolute temperatures (1/T) is indicated by a straight line (Fig. 2, they are analogous with those in W/WO_2 and WO_2/W_2O_5)[11]. Consequently, they can be expressed by the general equation of first order of the reaction isochore

$$\log K_p = -\frac{Q}{4.571\,T} + C.$$

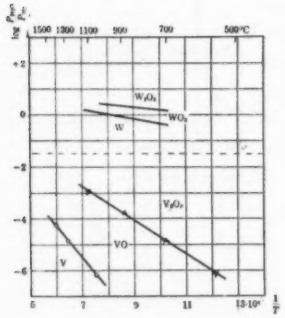

Fig. 2.

Thermodynamical Calculations.

From the values given in the above Table 2 a) and b) the following empirical equations for straight lines can be derived:

(11) L. Wöhler & R. Günther, *Z. Elektrochem.*, **29** (1923), 276;
L. Wöhler, Z. Shibata & R. Kunst, *Z. Elektrochem.*, **38** (1932), 808.

$$V/VO: \quad \log K_{p\cdot 1} = -\frac{12333}{T} + 3.141$$

$$VO/V_2O_3: \quad \log K_{p\cdot 2} = -\frac{6482}{T} + 1.747.$$

By the equation $\log K_p = -\frac{Q}{4.571\,T} + C$, in which $-\frac{Q}{4.571} = tg\,\alpha$ in the equation of first order, it follows that Q'_1 and Q'_2, the heat of the reactions (I) and (II), are obtained as the product of –4.571 with –12333 and –6482, respectively: that is,

$$V + H_2O = VO + H_2 + Q_1' (= 56.4 \text{ Cal.})$$

$$2VO + H_2O = V_2O_3 + H_2 + Q_2' (= 29.6 \text{ Cal.})$$

By combining the above empirical equations with the equation for dissociation of water vapour, the dissociation pressures of the vanadium oxides can be calculated;

$$K'_{p_{H_2O}} = \frac{p^2_{H_2} \cdot p_{O_2}}{p^2_{H_2O}} = \frac{1 \cdot p_{O_2}}{K_p^2}, \quad \text{thus} \quad p_{O_2} = K'_{p_{H_2O}} \cdot K_p^2 .$$

(III) $2VO \rightleftarrows 2V + O_2 + Q_1$;

O_2-pressure $= p_1 = K'_{p_{H_2O}} \cdot K^2_{p\cdot 1}$,

(IV) $2V_2O_3 \rightleftarrows 4VO + O_2 + Q_2$;

O_2-pressure $= p_2 = K'_{p_{H_2O}} \cdot K^2_{p\cdot 2}$.

By applying equation for dissociation of water[11] which, although approximate, is useful, $\log K'_{p_{H_2O}} = -\frac{26000}{T} + 6.06$, we obtain

$$\log p_1 = -\frac{26000}{T} + 6.06 + 2\left(-\frac{12333}{T} + 3.141\right)$$

$$= -\frac{50666}{T} + 12.342 \quad \text{atm. press.}$$

and similarly

$$\log p_2 = -\frac{38964}{T} + 9.554 \quad \text{atm. press.}$$

By the most general form of equation for vapour pressure, $\log p = -\frac{Q}{4.571T} + C$, approximate heat tonings Q_1 and Q_2 of the reactions (III) and (IV) can be calculated. That is,

$$Q_1 = -50666 \cdot -4.571 = 231.6 \text{ Cal.}$$

$$Q_2 = -38964 \cdot -4.571 = 178.1 \text{ Cal.}$$

or, the heat of the reactions:

$$2V + O_2 = V_2O_2 + Q_1 \ (= 231.6 \text{ Cal.})$$

$$V_2O_2 + 1/2\, O_2 = V_2O_3 + 1/2\, Q_2 \ (= 89.0 \text{ Cal.})$$

and by addition

$$2V + 3/2\, O_2 = V_2O_3 + Q_3 \ (= Q_1 + 1/2\, Q_2 = 320.6 \text{ Cal.})$$

Although the approximate value of heat of oxidation Q_1 of vanadium to its dioxide is little higher than that calculated by R. E. Slade & G. I. Higson[12] and that determined by W. G. Mixter, it was very close to their values. Heat of oxidation Q_3 of vanadium to its trioxide is found between those determined by Mixter and O. Ruff & L. Friedrich[13]; but of the two it was closer to that of Ruff & Friedrich. The values obtained by the author and the others mentioned above are given below for comparison:

	Author	Mixter	Ruff and Friedrich	Slade and Higson
Q_1	231.6	greater than 209[14]	—	222.0
Q_3	320.6	,, 353[15]	302±10	—

Since the values obtained closely agree with the others, it becomes obvious that the equilibria dealing here are correct, that is to say, the following reactions will undoubtedly take place,

$$V + H_2O \rightleftarrows VO + H_2$$

and

$$2VO + H_2O \rightleftarrows V_2O_3 + H_2 .$$

(12) *J. Chem. Soc.*, **115** (1919), 205.

(13) *Z. anorg. Chem.*, **89** (1914), 279.

(14) and (15) Calcd. according to Mixter's data; *Sill. Journ.* **34** (1912), 148; *Z. anorg. Chem.*, **78** (1912), 221.

Further, by applying Siegel's exact equation[16] for dissociation of water vapour, $[\log K_c = \frac{-24900}{T} + 1.335 \log T - 9.65 \cdot 10^{-5} T + 1.37 \cdot 10^{-7} T^2 - 6.65 \cdot 10^{-11} T^3 + 1.907 \cdot 10^{-18} T^5 - 1.08]$ the dissociation pressures of the two oxides at various temperatures are calculated as follows:

O_2-pressure at atmospheric.

abs. temp.	p_1(V/VO)	p_2(VO/V_2O_3)
823	—	$2.47 \cdot 10^{-37}$
983	—	$1.49 \cdot 10^{-29}$
1163	—	$2.69 \cdot 10^{-23}$
1325	$2.13 \cdot 10^{-25}$	—
1385	—	$3.94 \cdot 10^{-18}$
1541	$5.97 \cdot 10^{-20}$	—
1670	$1.80 \cdot 10^{-17}$	—
3610	—	1.0
3720	1.0	—

It will be noticed from the table that the oxygen pressure of trioxide will be one atmosphere at about 3610° abs., and that of dioxide at about 3720° abs.

The Free Energy and Heat of Formation of VO. Using the following heat capacities of substances

for VO; $C_p = 10.2$[17]

,, H_2; $C_p = 6.50 + 0.0009\,T$[18]

,, V; $C_p = 6.2$[17]

,, H_2O (g); $C_p = 8.81 - 0.0019\,T + 0.00000222\,T$[18]

being involved in the reaction,

$$V + H_2O = VO + H_2,$$

the general equation for heat of formation and free energy equation can be given as follows:

(16) W. Siegel, *Z. Physik. Chem.*, **87** (1914), 641.
(17) Calcd. by Kopp's rule; cf. Noyes & Sherrill, "Chem. Principle," (1930), 93.
(18) Lewis & Randall, "Thermodynamics," (1923), 80.

$$\text{(A)} \quad \Delta H = \Delta H_0 + 1.69\,T + 0.0014\,T^2 - 0.00000074\,T^3$$

$$\text{(B)} \quad \frac{\Delta F^0}{T} = \frac{\Delta H_0}{T} - 1.69 \ln T - 0.0014\,T + 0.00000037\,T^2 + I\,.$$

In the latter equation the values of ΔH_0 and I are obtained by an application of the relation

$$\Delta F^0 = -RT \ln K_p\,,$$

in which the values of K_p are known, as shown in Table 2 a),

$$\Delta H_0 = -59526 \text{ cal}, \quad I = 30.09$$

Substituting these values in (A) and (B),

$$\Delta H = -59526 + 1.69\,T + 0.0014\,T^2 - 0.00000074\,T^3$$

$$\frac{\Delta F^0}{T} = \frac{-59526}{T} - 1.69 \ln T - 0.0014\,T + 0.00000037\,T^2 + 30.09\,.$$

Solving for T at 298°, we find

$$\Delta F^0_{298} = -53543 \text{ cal}, \quad \Delta H_{298} = -58918 \text{ cal},$$

Combining the values of $\Delta F^0_{298} = -54507$ cal[19] and $\Delta H_{298} = -57820$ cal[20] for the free energy and heat of formation of water vapour from its element, the free energy and heat of formation of VO from its element can be calculated as follows:

$$\mathrm{V + H_2O = VO + H_2}\ ;\ \Delta F^0_{298} = -53543 \text{ cal},\ \Delta H_{298} = -58918 \text{ cal}.$$

$$\mathrm{H_2 + 1/2\,O_2 = H_2O(g)}\ ;\ \Delta F^0_{298} = -54507 \text{ cal},\ \Delta H_{298} = -57820 \text{ cal}.$$

hence $\mathrm{V + 1/2\,O_2 = VO}$; $\Delta F^0_{298} = -108050$ cal, $\Delta H_{298} = -116738$ cal.

or (i) $\mathrm{2V + O_2 = V_2O_2}$; $\Delta F^0_{298} = -216100$ cal, $\Delta H_{298} = -233476$ cal.

The final value –233476 cal, the heat of formation of V_2O_2 from its element, is nearly equivalent to the approximate value $Q_1 = 231.6$ Cal, for the corresponding heat of formation already obtained, in which it has been calculated by neglecting the change in heat capacities with temperature.

(19) Lewis & Randall, "Thermodynamics," (1923) p. 485.
(20) ibid. p. 477.

The Free Energy and Heat of Formation of V_2O_3. In the same manner as in the preceding section the general equations for heat of formation and also for free energy are derived for the reaction

$$2VO + H_2O = V_2O_3 + H_2;$$

From the heat capacities of these substances:

$$\begin{aligned} V_2O_3 \quad &; \quad C_p = 24.4^{(17)} \\ H_2 \quad &; \quad C_p = 6.50 + 0.0009\,T \\ 2VO \quad &; \quad C_p = 20.4^{(17)} \\ H_2O\,(g) \; &; \quad C_p = 8.81 - 0.0019\,T + 0.00000222\,T^2, \end{aligned}$$

are derived

$$\Delta H = \Delta H_0 + 1.69\,T + 0.0014\,T^2 - 0.00000074\,T^3$$

$$\frac{\Delta F^0}{T} = \frac{\Delta H_0}{T} - 1.69 \ln T - 0.0014\,T + 0.00000037\,T^2 + I.$$

Solving, we find

$$\Delta H_0 = -32124 \text{ cal.} \quad I = 23.22,$$

we may write,

$$\Delta H = -32124 + 1.69\,T + 0.0014\,T^2 - 0.00000074\,T^3$$

$$\frac{\Delta F^0}{T} = \frac{-32124}{T} - 1.69 \ln T - 0.0014\,T + 0.00000037\,T^2 + 23.22.$$

Hence

$$2VO + H_2O = V_2O_3 + H_2; \quad \Delta F^0_{298} = -28189 \text{ cal}, \quad \Delta H_{298} = -31516 \text{ cal.}$$

$$H_2 + 1/2\,O_2 = H_2O\,(g) \quad ; \quad \Delta F^0_{298} = -54507 \text{ cal}, \quad \Delta H_{298} = -57820 \text{ cal.}$$

hence

(ii) $$2VO + 1/2\,O_2 = V_2O_3 \quad ; \quad \Delta F^0_{298} = -82696 \text{ cal}, \quad \Delta H_{298} = -89336 \text{ cal.}$$

The final value –89336 cal, the heat of formation of V_2O_3 from VO and oxygen is equal to the approximate value $Q_2/2 = 89.0$ Cal, for the corresponding heat of formation already described.

Lastly, from the values (i) and (ii) are calculated the free energy and heat of formation of V_2O_3 from its element:

$$2VO+1/2\,O_2 = V_2O_3\ ;\quad \Delta F^0_{298} = -82696 \text{ cal},\quad \Delta H_{298} = -89336 \text{ cal}.$$

$$2V+O_2 = 2VO\ ;\quad \Delta F^0_{298} = -216100 \text{ cal},\quad \Delta H_{298} = -233476 \text{ cal}.$$

hence

$$2V+3/2\,O_2 = V_2O_3\ ;\quad \Delta F^0_{298} = -298796 \text{ cal},\quad \Delta H_{298} = -322812 \text{ cal}.$$

This final value, –322812 cal, the heat of formation of V_2O_3 from its element is also nearly equal to the approximate value $Q_3 = 320.6$ Cal, for the corresponding heat of formation already obtained.

In conclusion the writer wishes to express his sincere thanks to Prof. Dr. Keizô Iwasé, under whose guidance this work has been carried out and also to Dr. Shin-ichi Aoyama for his kind advice he has extended in carrying out this work.

Summary.

1. The vanadium-water vapour equilibria on the phase V/VO and VO/V_2O_3 have been determined over the range $p_{H_2O}=1.07\cdot10^{-3}$ to $6.65\cdot10^{-7}$ atmospheric pressure by the method of H. v. Wartenberg and S. Aoyama.

2. From the measured equilibrium temperatures and the corresponding K_p-values, it has been derived the general equations of the reaction isochore $\log K_p = -\frac{Q}{4.571\,T}+C$ for the two systems:

$$V/VO\ ;\quad \log K_{p\cdot1} = -12333/T+3.141$$

$$VO/V_2O_3;\quad \log K_{p\cdot2} = -6482/T+1.747,$$

and from these the approximate heat of reaction have been calculated:

$$V+H_2O = VO+H_2+Q'_1(=56.4 \text{ Cal.})$$

$$2VO+H_2O = V_2O_3+H_2+Q'_2(=29.6 \text{ Cal.})$$

3. Combining the above equations with the equation for dissociation of water vapour, the general equations for dissociation of vanadium oxides have been derived, and from these it has been calculated O_2-pressures for several temperatures and approximate values for the heat of formation of VO from V, of V_2O_3 from VO, and of V_2O_3 from V:

$$2V+O_2 = V_2O_2+231.6 \text{ Cal.}$$

$$2VO+1/2\,O_2 = V_2O_3+89.0 \text{ Cal.}$$

$$2V+3/2\,O_2 = V_2O_3+320.6 \text{ Cal.}$$

4. By the use of the equations for heat capacities of substances being involved in each reaction, the free energies and heats of formation have been calculated at 25°C.; that of VO from its element and that of V_2O_3 from its element and also from VO and oxygen:

$$2V+O_2=V_2O_2 \quad ; \quad \Delta F^0_{298}=-216100 \text{ cal}, \quad \Delta H_{298}=-233476 \text{ cal}.$$
$$2VO+1/2\,O_2=V_2O_3 ; \quad \Delta F^0_{298}=-82696 \text{ cal}, \quad \Delta H_{298}=-89336 \text{ cal}.$$
$$2V+3/2\,O_2=V_2O_2 \quad ; \quad \Delta F^0_{298}=-298796 \text{ cal}, \quad \Delta H_{298}=-322812 \text{ cal}.$$

The Research Institute for Iron, Steel and Other Metals,
Tohoku Imperial University, Sendai.

SOME APPLICATIONS IN THE POTENTIOMETRIC TITRATIONS BY USING VACUUM TUBE.

By **Kosaku MASAKI** and **Okiro HIRABAYASHI.**

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Introduction.

During the process of work in analysis, it is very necessary to execute a titration securely and swiftly. The potentiometric titrations in oxidation and reduction reactions by using a vacuum tube were reported by many investigators.(1) In all of these investigations, a negative potential is put on the grid with respect to the filament and the indicator electrode is directly connected to the grid; for example the indicator elcctrode is platinum and the calomel electrode is connected to the battery impressing the negative potential to the grid. By this method it is necessary to plot $\Delta E/\Delta V$ to obtain the equivalence point, where ΔE is a small change of the e.m.f. of the cell during titration and ΔV is the volume of the titrating solution. The values of galvanometer or milliammeter defections may be used in place of ΔE. Recently J. L. Kassner, R. B. Hunze

(1) Goode, *J. Amer. Chem. Soc.*, **44** (1922), 26; **47** (1925), 2483.
Calhane and Cushing, *J. Ind. Eng. Chem.*, **15** (1923), 1118.
Treadwell, *Hel. Chem. Acta.*, **8** (1925), 89.
Williams and Whitenack, *J. Physik. Chem.*, **31** (1927), 519.
Morton, *Pharm. J.*, **118** (1927), 761.
E. Beri, W. Herbert und W. Wohlig, „Die Chem. Fabrik," 1930, 445; 448.

and J. N. Chatfield[2] studied the method to avoid the complication of plotting curves to obtain the equivalence point. It was reported that their method was preferable in the electrometric titrations of some oxidation-reduction reactions. The present investigation was started to find out the characteristics of the apparatus modified by the author, when it was applied on the electrometric titrations of many oxidation-reduction reactions.

Apparatus.

The circuit of the apparatus is shown in Fig. 1, in which the details of every parts are as follows. V in circle is voltmeter reading in units of 0.1 volt. D is potential divider of 10,000 ohms. C is 4-volt battery, A 6-volt storage battery and B 45-volt dry-battery. W is 30-ohm variable resistance. R is 10,000-ohm variable resistance. A in circle is milliammeter reading 500 milliamperes. T is Mazda vacuum tube, UX 201A, whose filament is operated normally with 5 volts, drawing 0.25 ampere. G is galvanometer, whose rating is as follows; made by Yokokawa, Type D_2, Class L, Sensibility 5×10^{-8}-Ampere, 6.8×10^{-5}-volt, Period 3 seconds, galvanometer resistance 300-ohm. C and c′ are platinum electrodes, 0.4 mm. in diameter and 40 cm. of length. P is shunt resistance, 5,000, 10,000, 20,000 and 30,000-ohms. K shown in Fig. 1 is the reaction vessel which is a beaker or an Erlenmeyer flask of about 200 c.c. But in accurate titrations, it is necessary to use the apparatus designed by Hostetter and Roberts.[3] Ours is shown in Fig. 2. Reaction vessel is made of glass, 6 cm. in diameter and 13 cm. in length. From G carbon dioxide is passed into the vessel. S is a stirrer driven by a motor. Additions of a solution in a small quantity were carried out by the aid of slender glass rod L.

In potentiometric titrations, up to the present, a negative potential is impressed on the grid of the vacuum tube, while the apparatus shown in Fig. 1 differs from other's in that a positive potential is placed on the grid with respect to the filament of the vacuum tube. Accordingly, the grid current, which is very small due to the construction of the vacuum tube, flows through the titrating cell and has been employed to polarize bimetallic platinum electrodes which have been substituted for the monometallic system. The theory of polarized electrodes has been studied by

(2) J. L. Kassner, R. B. Hunze and J. N. Chatfield, *J. Amer. Chem. Soc.*, **54** (1932), 2278.

(3) Hostetter and Roberts, *J. Amer. Chem. Soc.*, **41** (1919), 1337.

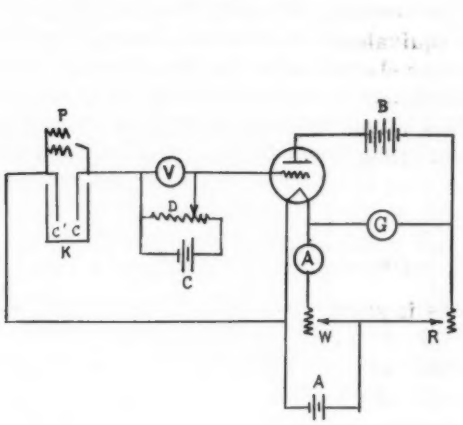

Fig. 1.

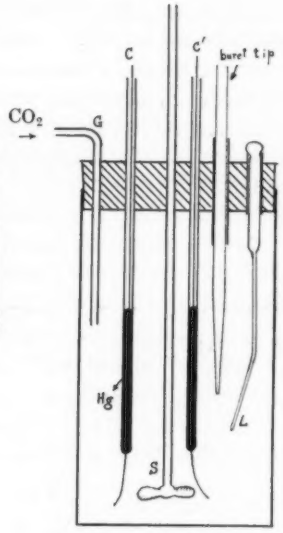

Fig. 2.

Willard and Fenwick[4] and Van Name and Fenwick.[5] They have shown that polarized electrodes owe their effect in electrometric titration to gas reaction taking place on the surface of the electrodes and that the potential difference between the electrodes remains practically constant up to the equivalence point. Moreover, a part of the grid current is shunted to the bimetallic electrodes with shunt resistance P as shown in Fig. 1 for the successful operation of this apparatus. It is very necessary that the potential difference between the electrodes remains constant up to the equivalence point in order to operate this apparatus, and this has been accomplished by shunting a part of the polarizing current to the electrodes. Thus shunted electrodes were first used by Foulk and Bawden.[6] They stated no current flows through the solution when the drop in potential across the shunt is equal to the back e.m.f. due to polarization.

If the bimetallic platinum electrodes have been placed in the solution to be titrated and the resistance R adjusted so that the galvanometer reading is zero, then the potential at M and N would be the same. Electrons flow through the vacuum tube in three ciruits; namely, filament, filament to grid, and filament to plate. The electrons picked up

(4) *J. Amer. Chem. Soc.*, **44** (1922), 2504.
(5) Van Name and Fenwick, *J. Amer. Chem. Soc.*, **47** (1925), 9; 19.
(6) Foulk and Bawden, *J. Amer. Chem. Soc.*, **48** (1926), 2045.

by the plate may be considered as flowing through the B-battery, R, and back to the A-battery. The strength of this current depends upon the temperature of the filament which is controlled by the filament current varied with W, the voltage of the B-battery, the value of R, and the potential impressed on the grid. The electrons picked up by the grid polarize the bimetallic platinum electrodes. The current in these three circuits will remain constant during the course of a titration as long as the potential difference between c and c′ remains constant if the other adjustments are not changed. A slight change in the potential between c and c′ will produce a corresponding change in the potential impressed on the grid, and this will produce a relatively large change in the plate current by the characteristics of the vacuum tube. Accordingly the balance at M and N is disturbed and it causes the deflection of the needle of the galvanometer.

Experimental.

The preparations of the solutions used were as follows. The reagents used were from Kahlbaum.

(1) Sodium thiosulphate is purified by recrystallization. About 26 gr. of it are weighed out and diluted to about 1 litre. The solution is standardized indirectly by titration with potassium bichromate. Dissolve 5 gr. KI and 4 gr. $NaHCO_3$ in 500 c.c. H_2O in an Erlenmeyer flask at room temperature and add HCl slowly, shaking the flask, until there is no more evolution of CO_2 and then add about 10 c.c. more of the acid, and 35 c.c. of 0.1 N. $K_2Cr_2O_7$. After mixing the solution, rinse the sides of the flask with a few c.c. of water, allowing it to form a layer over the solution without mixing; stopper the flask and allow to stand about 10 minutes. Then with thorough mixing run in thiosulphate until the solution is slightly yellow, add a few drops of starch solution and continue to add slowly the thiosulphate solution until the bright blue colour disappears and only the pale green colour of $CrCl_3$ remains.

(2) Potassium bichromate is purified by recrystallization and dried in an air oven, 4.9035 gr. of it are exactly weighed out and dissolved to 1 litre.

(3) Iodine. Dissolve about 13.5 gr. of pure iodine in a solution of 24 gr. of KI in 200 c.c. of H_2O and dilute to 1 litre. This solution is standardized by thiosulphate using starch as indicator.

(4) Ferrous sulphate. Weigh out exactly 39.214 gr. of ferrous sulphate and dissolve in dilute sulphuric acid (sp. gr. 1.2) to 1 litre.

(5) Potassium permanganate. Dissolve 3.3 gr. of $KMnO_4$ in 1 litre of distilled water and allow to stand a day. This is standardized by sodium oxalate extremely pure and dry.

(6) Potassium cyanide. Weigh out about 8 gr. and dissolve in 1 litre H_2O. This is standardized by 0.1 N. standard $AgNO_3$.

(7) Potassium bromate. Weigh out exactly 16.701 gr. and dilute to 1 litre exactly.

(8) Potassium iodide is purified by recrystallization and dried in air oven. Weigh out exactly 16.603 gr. and dilute to 1 litre.

(9) Potassium iodate. Weigh out exactly 4.2806 gr. and dissolve to 1 litre.

It was thought at first that it would be necessary to control the shunt to obtain good results with this apparatus, but in practice it was often not necessary. The results of the titrations using different shunts are shown in Table 1. The calculated value of c.c. of 0.1 N. sodium thiosulphate is the average of five determinations using starch as the indicator.

Table 1.

Titrations of approximately 0.1 N. iodine solution with sodium thiosulphate.[7]
V: 1.5 volts; A: 0.25 ampere; B: 45 volts.

Run	P:ohms	Sodium thiosulphate		
		c.c. calc.	c·c. found	c.c. dif.
1	5.000	10.45	10.45	0.00
2	10.000	10.45	10.43	0.02
3	20.000	10.45	10.43	0.02
4	30.000	10.45	10.45	0.00
5	50.000	10.45	10.44	0.01

When no shunt resistance was employed the needle of the galvanometer drifted off the scale after the addition of about 1 c.c. of thiosulphate, and under certain circumstances even after one drop. It is distinct that the end-point obtained by this apparatus is slightly in advance of the end-point obtained by the starch.[8] In many titrations described below, P shunt resistance was used in the range shown above.

The galvanometer deflections during titrations, for example, are shown in Table 2, but in many cases there are no great difference.

(7) A. Schlfeichen, *Z. Anal. Chem.*, **65** (1925), 406.
(8) Foulk and Bawden, *J. Amer. Chem. Soc.*, **48** (1926), 2047.

Table 2.

Titration of approximately 0.1 N. iodine with sodium thiosulphate.

c.c. of 0.1 N.$Na_2S_2O_3$	Gal. def. (zero center)	c.c. of 0.1 N.$Na_2S_2O_3$	Gal. def. (zero center)
0.00	0.0	10.35	4.7 left
5.00	1.0 left	10.40	5.3 ,,
8.00	1.7 ,,	10.42	5.5 ,,
10.00	2.9 ,,	10.43	5.6 ,,
10.20	3.6 ,,	10.44	14.0 right
10.31	4.5 ,,		

Further, in order to show that it is not necessary to control the different variables in this apparatus within narrow limits the following data are presented (Table 3).

Table 3.

Titration of approximately 0.1 N. iodine with sodium thiosulphate.

Run	Sodium thiosulphate c.c. calc.	c.c. found	c.c. dif.	Filament Current ampere	V volts	P ohms
1	24.40	24.39	0.01	0.25	2.0	30.000
2	24.40	24.40	0.00	0.20	2.0	30.000
3	24.40	24.40	0.00	0.22	2.0	30.000
4	24.40	24.41	0.01	0.25	1.7	20.000
5	24.40	24.40	0.00	0.25	1.6	30.000
6	24.40	24.39	0.01	0.20	2.2	35.000
7	24.40	24.38	0.02	0.22	1.5	20.000
8	24.40	24.40	0.00	0.25	1.2	15.000
9	24.40	24.38	0.02	0.25	1.0	20.000
10	24.40	24.38	0.02	0.20	1.0	20.000
11	24.40	24.40	0.00	0.25	1.0	10.000
12	24.40	24.39	0.01	0.20	1.0	10.000

B-battery is 45 volts.

As is shown in Fig. 2, one of the platinum electrodes is placed close under the burette, so that there will be temporarily a slight difference in the composition of the solution when the drops of a titrating solution is added. And the deflection of the needle of the galvanometer will be also

temporarily unstable and great. But it again becomes stable if the addition of the titrating solution is interrupted. Thus the approach of the end-point is indicated.

Results of some applications in oxidation-reduction reactions using this apparatus are given in the following tables.

As an additional characteristic in this apparatus, there is the indication of the approach of the end point.

Table 4.

Titration of ferrous sulphate with potassium permanganate.

V: 1.5 volts; A: 0.20 ampere; P: 20.000 ohms; B: 45.0 volts.

Run	c.c. calc.	c.c. found	c.c. dif.
1	22.94	22.89	0.05
2	22.94	22.89	0.05
3	22.94	22.90	0.04
4	22.94	22.88	0.06
5	22.94	22.89	0.05

V: 1.0 volt; A: 0.25 ampere; P: 25.000 ohms; B: 45 volts.

1	22.94	22.89	0.05
2	22.94	22.88	0.06
3	22.94	22.89	0.05

The calculated values are the average of five determinations when the solution to be titrated is coloured pink.

Table 5.

Titration of iodine with potassium cyanide.

V: 0.7 volt; A: 0.21 ampere; P: 20.000 ohms; B: 45 volts.

Run	c.c. calc.	c.c. found	c.c. dif.
1	12.84	12.75	0.09
2	12.84	12.76	0.08
3	12.84	12.76	0.08
4	12.84	12.76.	0.08
5	12.84	12.76	0.08

The c.c. calculated is the average of five determinations using starch as indicator.

The following experiments were carried out to test the possibility of the titrations of some oxidation-reduction reactions, though the c.c. calculated is not so accurate as the value obtained from the weight of reagents.

Table 6.

Titration of ferrous sulphate with 0.1 N. potassium bichromate.

V: 0.8 volt; A: 0.20 ampere; P: 20.000 ohms; B: 22.5 volts.

Run	c.c. calc.	c.c. found	c.c. dif.
1	23.12	23.10	0.02
2	23.12	23.11	0.01
3	23.12	23.11	0.01

Table 7.

Titration of ferrous sulphate with 0.1 N. potassium bromate.

V: 1.4 volts; A: 0.20 ampere; P: 10.000 ohms; B: 45 volts.

Run	c.c. calc.	c.c. found	c.c. dif.
1	8.17	8.18	0.01
2	8.17	8.17	0.00
3	8.17	8.18	0.01

Table 8.

Titration of potassium iodide with 0.1 N. potassium bichromate.

V: 0.8 volt; A: 0.20 ampere; P: 10.000 ohms; B: 22.5 volts.

Run	c.c. calc.	c.c. found	c.c. dif.
1	25.00	24.96	0.04
2	25.00	24.95	0.05
3	25.00	24.95	0.05

In this case, the galvanometer deflection is very unstable and the titration becomes difficult. Above data are only the most likely results selected among many titrations.

Table 9.

Titration of potassium iodide with 0.1 N. potassium bromate.

V: 1.0 volt; A: 0.25 ampere; P: 20.000 ohms; B: 45 volts.

Run	c.c. calc.	c.c. found	c.c. dif.
1	25.00	25.05	0.05
2	25.00	25.07	0.07
3	25.00	25.06	0.06

Table 10.

Titration of potassium iodide with potassium permanganate.

V: 2.0 volts; A: 0.25 ampere; P: 25.000 ohms; B: 45 volts.

Run	c.c. calc.	c.c. found	c.c. dif.
1	23.30	23.27	0.03
2	23.30	23.25	0.05
3	23.30	23.25	0.05

In this case, the galvanometer deflection is exceptional and the end-point is very apparent.

Table 11.

c.c. of $KMnO_4$	gal. deflection	c.c. of $KMnO_4$	gal. deflection
0.00	0.0	23.10	18.1 left
10.00	10.4 left	23.20	18.1 ,,
20.00	17.7 ,,	23.23	18.0 ,,
22.00	18.1 ,,	23.24	18.1 ,,
23.00	18.1 ,,	23.25	to right extremely

Table 12.

Titration of potassium iodide with 0.1 N. potassium iodate.

V: 1.5 volts; A: 0.20 ampere; P: 20.000 ohms; B: 45 volts.

Run	c.c. calc.	c.c. found	c.c. dif.
1	25.00	24.89	0.11
2	25.00	24.80	0.20
3	25.00	24.80	0.20

Table 13.

Titration of potassium permanganate with potassium ferrocyanide.

V: 0.6 volt; A: 0.20 ampere; P: 10.000 ohms; B: 45 volts.

Run	c.c. calc.	c.c. found	c.c. dif.
1	23.19	23.00	0.19
2	23.19	22.99	0.20
3	23.19	22.99	0.20

Author wishes to express his thanks to Prof. K. Kido who gave him the reagents.

Summary.

In the above investigation, the polarized platinum electrodes by means of grid current, which is obtained by impressing a positive potential on the grid, were used in the potentiometric titrations. In this apparatus, the approach of the end point is indicated, thus the neither plotting or recording nor adjustments is necessary during the titration; but it is necessary to control the positive potential impressed on the grid at the beginning of the titration lest the needle of galvanometer will kick off. The agreement between the calculated and found values is very good in each case.

Yokohama Higher Technical School,
Yokohama.